

# NOVEL SOLID SORBENTS FOR CARBON DIOXIDE CAPTURE

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**Abstract:** Capture and separation of carbon dioxide from large point sources is a key step in the overall CO<sub>2</sub> sequestration process. An improvement of the separation and capture of CO<sub>2</sub> will thus reduce the total cost required for sequestration. NETL has recently initiated a study to develop novel amine enriched solid sorbents for the capture of CO<sub>2</sub>. This concept is to prepare the solid sorbents via chemical treatment of the surface oxide of the high surface area materials with various amine compounds. Preliminary results indicate that the amine-enriched sorbents show a capability for capture/release of CO<sub>2</sub>, and the sorbents are regenerable.

**Key words:** solid sorbents, carbon dioxide capture

## 1. INTRODUCTION

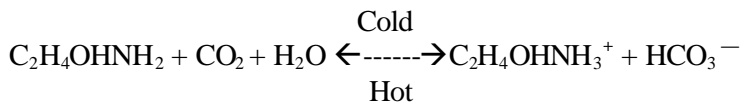
One of the most alarming global environmental problems of today, is the projected increase of the natural greenhouse effect resulting from increased production of greenhouse gases. Over the last decade, we have been deluged with reports from scientists worldwide, detailing the accumulation of greenhouse gases in the atmosphere, the most important of which is CO<sub>2</sub>, and its associated role in causing global climate warming. In the 1980's, carbon dioxide-containing flue gases contributed up to 25% of the global CO<sub>2</sub> emission and were responsible for 14% of the estimated global

warming. Analyses of the exhaust gases from various U.S. power stations concluded carbon dioxide concentrations ranged from 13% up to 27%.<sup>1</sup> In order for C-rich fossil fuels, i.e., coal and natural gas, to remain a viable and environmentally acceptable energy source for the 21st century, technologies implementing capture and sequestration, utilization, or recycling of carbon dioxide need to take precedence.

A number of recent concepts have been offered as reasonable destinations of carbon dioxide from the combustion of fossil fuels. Options for storing CO<sub>2</sub> captured from industrial plants include the deep ocean, depleted natural gas field and oil wells, biomass, salt domes and deep saline aquifers. Separation and capture of CO<sub>2</sub> have been identified as a high-priority research topic in several DOE reports.<sup>1,2</sup> The costs of separation and capture, including compression to the required pressure for the sequestration step are generally estimated to comprise about three-fourths of the total cost of ocean or geologic sequestration. An improvement of the separation and capture of CO<sub>2</sub> will reduce the total cost required for sequestration.

The goal of CO<sub>2</sub> separation and capture is to isolate CO<sub>2</sub> from its many sources in a form suitable for transport and sequestration. The most likely options for CO<sub>2</sub> separation and capture include chemical absorption, physical and chemical adsorption, low-temperature distillation, gas-separation membranes, mineralization/biomineralization, and vegetation.

The CO<sub>2</sub> absorption process using aqueous amine solutions has been extensively used for the removal of CO<sub>2</sub> from gas streams in many industries. This process based on the principles of chemical absorption of CO<sub>2</sub> via monoethanolamine (MEA), diethanolamine (DEA), or methyldiethanolamine (MDEA) is considered to be a potential technique for capturing greenhouse gas emission from flue gas streams. Wet chemical stripping of CO<sub>2</sub> involves one or more reversible chemical reactions between CO<sub>2</sub> and another material such as MEA to produce a liquid species which, upon heating, breaks down to liberate CO<sub>2</sub>, and regenerate the original material used to react with CO<sub>2</sub>.<sup>3-5</sup>



The amines (MEA and DEA) are utilized in the aqueous phase, typically containing 25-30 wt% amine. The amine solution enters the top of an absorption tower while the carbon dioxide containing gaseous stream is

introduced at the bottom. While intimately contacting the gaseous stream in a countercurrent fashion, the amine solution chemically absorbs the carbon dioxide from the gaseous stream. Desorption of the adsorbed carbon dioxide then proceeds via a thermal regeneration process. During desorption, carbon dioxide and water evolve from the amine solution and are separated by condensing the water vapor in a heat exchanger. Once regenerated, the amine solution is recycled back to the absorption tower for additional carbon dioxide absorption.

A typical MEA capture of CO<sub>2</sub> from flue gas produced from coal combustion is likely to involve an energy penalty of about 35%, and this absorption is influenced by the availability of gas/liquid interaction surfaces (i.e., ceramic intalox saddles 1/4" have a contact area of 981 m<sup>2</sup>/m<sup>3</sup>). These processes are, in general, energy intensive. The energy intensity of these processes is related partly to their low capacity (CO<sub>2</sub> absorbed per unit mass). Therefore, a large volume of liquid is required to release a small amount of gas. Amine solution also has a limited lifetime due to degradation through oxidation of the amine. Oxygen present in the gas stream oxidizes the amine particularly during desorption when the sorbent is heated. In addition, corrosion problems are usually observed for the aqueous amine process.<sup>6</sup>

Energy savings can be achieved if a solvent/sorbent that has high absorption capacity at moderate temperatures and pressures can be developed. The higher the absorption capacity, the less quantity of solvent required to handle a given gas stream, and the less sensible and latent energy are required in the regeneration step. Therefore, new novel solvents/sorbents to reduce total capital and operating cost need to be developed.

Recently, several solids sorbents have been utilized to remove carbon dioxide from enclosed environments such as submarines, aircrafts, spacecrafts, and enclosed pressurized chambers.<sup>7-9</sup> Zinnen et al.,<sup>7</sup> reported that the adsorptive separation of carbon dioxide from air using a carbon molecular sieve-based material which has been functionalized with amine groups. CO<sub>2</sub> is contacted with carbon molecular sieves at room temperature and atmospheric pressure, with the adsorbed CO<sub>2</sub> being released by heating to 70°C. The treated carbon molecular sieve may be utilized for the treatment of air in a number of enclosed environments or vehicles, especially in the removal of carbon dioxide from breathing air. The adsorbed carbon dioxide may then be recovered from the carbon molecular sieves by conventional means such as depressurization, heating, or a combination of both methods that regenerate the material and returns it to an active or unsaturated form.<sup>7</sup> Birbara et al.,<sup>8</sup> reported using a supported amine-polyol

sorbent for CO<sub>2</sub> capture. Leal et al.,<sup>10</sup> demonstrated the reversible adsorption of CO<sub>2</sub> on amine surface-bonded silica gel. Recently, Birbara et al.,<sup>9</sup> reported to use a regenerable acrylic ester resin-based solid amine sorbent for CO<sub>2</sub> capture. The porous support provides the amine with structural integrity and a surface for gas/solid contact. The ability to regenerate an adsorbent and the ease of this regeneration are also important considerations. The need for extreme conditions such as high temperatures or very low vacuums makes regeneration more complicated and costly.<sup>7</sup>

The objective of this research is to develop novel amine enriched sorbents for the capture of CO<sub>2</sub> from flue gas streams generated by the utility industry. These novel CO<sub>2</sub> capture sorbents can be prepared by the chemical treatment of the high surface oxide surface materials (i.e., activated carbon with density of 2.3 g/cm<sup>3</sup> has a surface area of 400 m<sup>2</sup>/g and a contact area of 9.19 x 10<sup>8</sup> m<sup>2</sup>/m<sup>3</sup>) with various amine compounds (7-10). The implanting of amine groups on the high surface area material may increase the needed contact area between CO<sub>2</sub> and amine by several magnitudes. Furthermore, mass and heat-transfer problems could be reduced significantly by the novel concept of applying gas-amine enriched solid reactions for CO<sub>2</sub> capture versus that of gas-liquid reactions. Therefore, only a small amount of sorbent is needed for capturing the same amount of CO<sub>2</sub> versus that of the typical aqueous amine processes. Thus, a significant improvement in the efficiency of the process is realized due to increased contact area and less energy consumption for regenerating the adsorbents. In addition, the high surface area material can provide the physical/chemical adsorption function of CO<sub>2</sub> that might enhance the CO<sub>2</sub> capture process.

In this work, we report the in-situ FTIR/Temperature-Programmed-Desorption (TPD) studies of adsorption/absorption and desorption of CO<sub>2</sub> via a unique amine enriched sorbent, derived from fly ash.

## **2. EXPERIMENTAL**

The material tested in this study was a fly ash with 8% carbon content, labeled Sample 59. The sample was first concentrated via a column agglomeration technique to enhance the concentration of carbon to about 52 %, labeled Sample 95.<sup>11</sup> Sample 95 had a surface area of about 30 m<sup>2</sup>/g. Subsequently, three different amine treatment methods were applied to sample 95. The treated amine-enriched samples were designated as 95A, 95B and 95C.<sup>7-10</sup>

In order to understand the reaction of CO<sub>2</sub> on these amine-enriched solids and assess their relative CO<sub>2</sub> uptake capabilities, adsorption studies followed by a temperature programmed desorption (TPD) technique were conducted under ambient pressure and at temperatures between 30 and 120 °C. Figure 1 illustrates a schematic of the experimental system. All gas flows to the system were regulated with Brooks 5850 mass flow controllers. The 4-port valve allowed for ease of switching between He and 10% CO<sub>2</sub>/He flows to the reactor system; moisture was added to either flow stream via a water saturator maintained at ambient temperature (partial pressure of H<sub>2</sub>O = 23.36 mmHg). A sample charge of 100 mg was used in each experiment; approximately 15 mg was placed into a Spectra Tech diffuse reflectance infrared Fourier transform infrared spectroscopy (DRIFTS) reactor while the remaining sample was charged to a tubular reactor connected to the effluent of the DRIFTS. Separate temperature control systems existed on each reactor. The sample in the DRIFTS reactor was examined in situ via a Nicolet Magna 560 infrared spectrometer (IR), allowing observation of CO<sub>2</sub> adsorbate formation/desorption on the sample surface. The gaseous effluent from the DRIFTS-tubular reactor was continuously analyzed by a Balzers QMG 112 mass spectrometer (MS), allowing determination of the CO<sub>2</sub> concentration in the effluent stream. Capture capacities of the different amine-enriched samples were calculated by MS analysis of the CO<sub>2</sub> (m/e = 44) desorption profile.

Each sample was first exposed to He at a flow rate of 30 ml/min for 3 hours, prior to any further experiment, to clean the sample surface (confirmed by observing stable background signals of both IR and MS). For the CO<sub>2</sub> absorption study, He flow was then replaced with 10% CO<sub>2</sub> in He at ambient conditions. The moisture content plays an important role in the CO<sub>2</sub> adsorption process; formation of CO<sub>2</sub>-amine complexes take place only in its presence. Therefore, after the exposure to 10% CO<sub>2</sub> in He, the flow was redirected through an H<sub>2</sub>O saturator; the CO<sub>2</sub>/H<sub>2</sub>O/He flow over the surface of the sample was maintained for 30 minutes. The CO<sub>2</sub>/H<sub>2</sub>O/He stream was then replaced by H<sub>2</sub>O/He flow to expunge the system of gaseous CO<sub>2</sub>.

For the TPD study, the H<sub>2</sub>O/He flow was finally replaced with pure He flow to monitor desorption of adsorbed CO<sub>2</sub>. Both reactors were heated, simultaneously, from 30 to 120°C at a rate of 10 °C/min and maintained at 120 °C for an additional 20 min. CO<sub>2</sub> desorption amounts were calculated by separate calibration factors that were obtained during each experiment. The calibration factors were obtained by pulsing 1 cc volumes of the 10% CO<sub>2</sub>/He (4.089 µmol CO<sub>2</sub>) directly to the MS using a 6-port valve. The CO<sub>2</sub>

pulse profile ( $m/e = 44$ ) was integrated and a calibration factor was calculated, equating areas to moles of  $\text{CO}_2$ . Using this calibration factor, the integrated  $\text{CO}_2$  desorption curve could be converted into moles of  $\text{CO}_2$  eluted.

Sample regeneration was also assessed via reusing a sample following its adsorption/desorption techniques. Following the TPD, the sample was cooled to ambient temperature and its surface was again cleansed via He flow for 3 h. This was followed by conducting the adsorption and desorption techniques, described above, again.

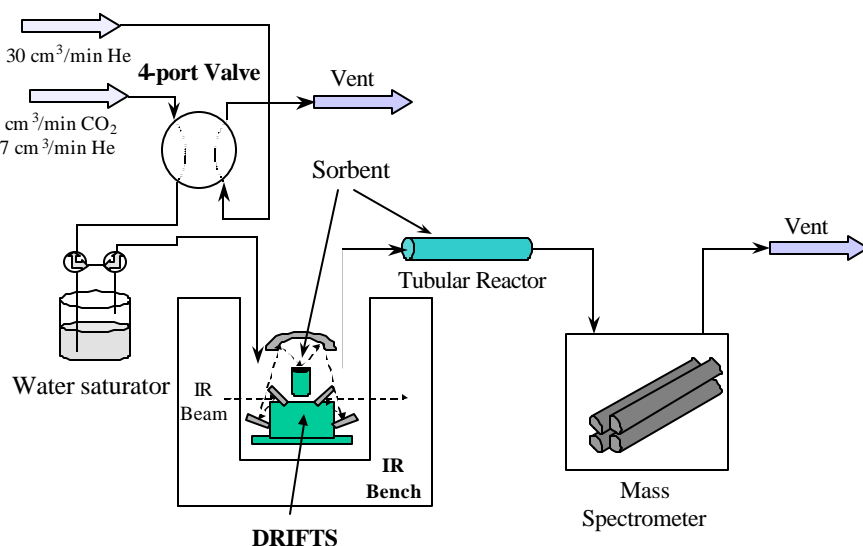


Figure 1. [Schematic of experimental system]

### 3. RESULTS AND DISCUSSION

The detailed chemical analyses of the amine-enriched sorbents along with the untreated samples are illustrated in Table 1. A significant increase of nitrogen contents from 0.60 to 0.73% was observed on the treated samples. In addition, the oxygen contents also increase to a great extent from 0.77 to as high as 2.81% on the enriched amine samples. The increase of the nitrogen contents on the treated samples suggested that some nitrogen-containing species were attached and/or bonded to the treated samples. This implies presence of amine species on the treated samples.

A typical adsorption profile as analyzed by DRIFTS is shown in Figure 2. Exposure of the surface to dry CO<sub>2</sub>/He flow did not lead to any observable surface CO<sub>2</sub>-amine complex formations; only gaseous CO<sub>2</sub> (doublet centered at 2350 cm<sup>-1</sup>) was observed. When the CO<sub>2</sub>/He flow was switched to CO<sub>2</sub>/H<sub>2</sub>O/He, two distinct bands, 1148 cm<sup>-1</sup> and 1087 cm<sup>-1</sup>, as well as a loss band at 1209 cm<sup>-1</sup> formed shortly thereafter. These bands were assigned tentatively to bidentate carbonate and monodentate carbonate, respectively, whereas the loss band is believed to represent a species displaced as a result of the CO<sub>2</sub> adsorption. After extended exposure a band appeared at 1649 cm<sup>-1</sup>, representative of H<sub>2</sub>O bending. Upon switching to He flow to purge gaseous CO<sub>2</sub>, the intensities of the adsorbed species were seen to decrease, indicating that the CO<sub>2</sub>-amine complex is not stable in the absence of H<sub>2</sub>O.

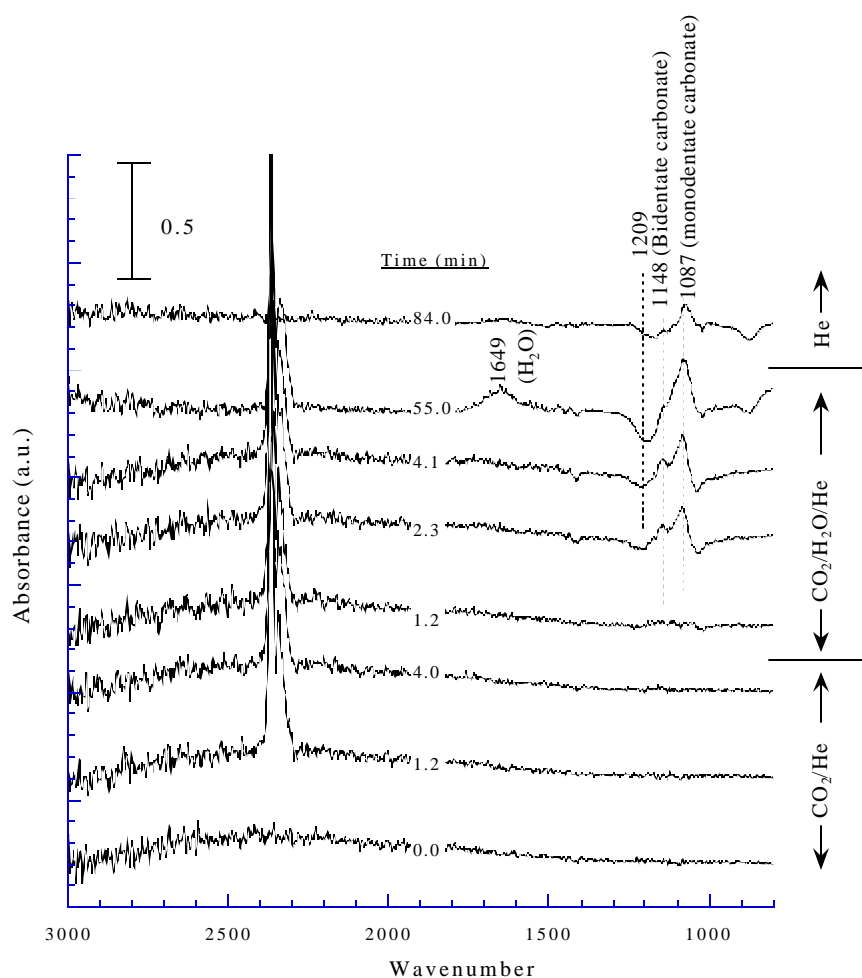


Figure 2. [IR analysis of CO<sub>2</sub> adsorption over 95C at ambient temperature. Feed gas compositions to the system are shown between brackets on the right; times indicated are relative to points of feed composition changes]

To prevent the desorption of amine-CO<sub>2</sub> complexes during the purging of gaseous CO<sub>2</sub>, the CO<sub>2</sub>/H<sub>2</sub>O/He stream was replaced with H<sub>2</sub>O/He instead of only He at the completion of the adsorption phase. This proved to be effective method to maintain adsorbates while purging the system of gaseous CO<sub>2</sub>. This finding led to the procedure described above where the TPD is conducted under only He but H<sub>2</sub>O/He is used to purge CO<sub>2</sub>. It is believed that the presence of moisture is beneficial to the long-term stability of the



subject material because the carbon dioxide-retaining complex requires the presence of a water molecule.<sup>7</sup> These procedures (using H<sub>2</sub>O/He instead of He only during the purging of gaseous CO<sub>2</sub>) were applied to all samples.

The MS results from the TPD study over 95°C are shown in Figure 3. Profiles at  $m/e = 18, 32, 44$ , and  $28$  correspond to H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>/CO, respectively. Two desorption peaks from the CO<sub>2</sub> profile, centered at 40 and 110 °C, were observed along with corresponding peaks within the H<sub>2</sub>O profile centered around 60 and 120 °C; these may correlate to the decomposition of CO<sub>2</sub>-amine complexes: monodentate carbonate and bidentate carbonate, respectively. Due to the premature CO<sub>2</sub> desorption in Figure 2, the experiment was repeated over a fresh sample employing the techniques discussed above to purge gaseous CO<sub>2</sub> while retaining all the captured CO<sub>2</sub>.

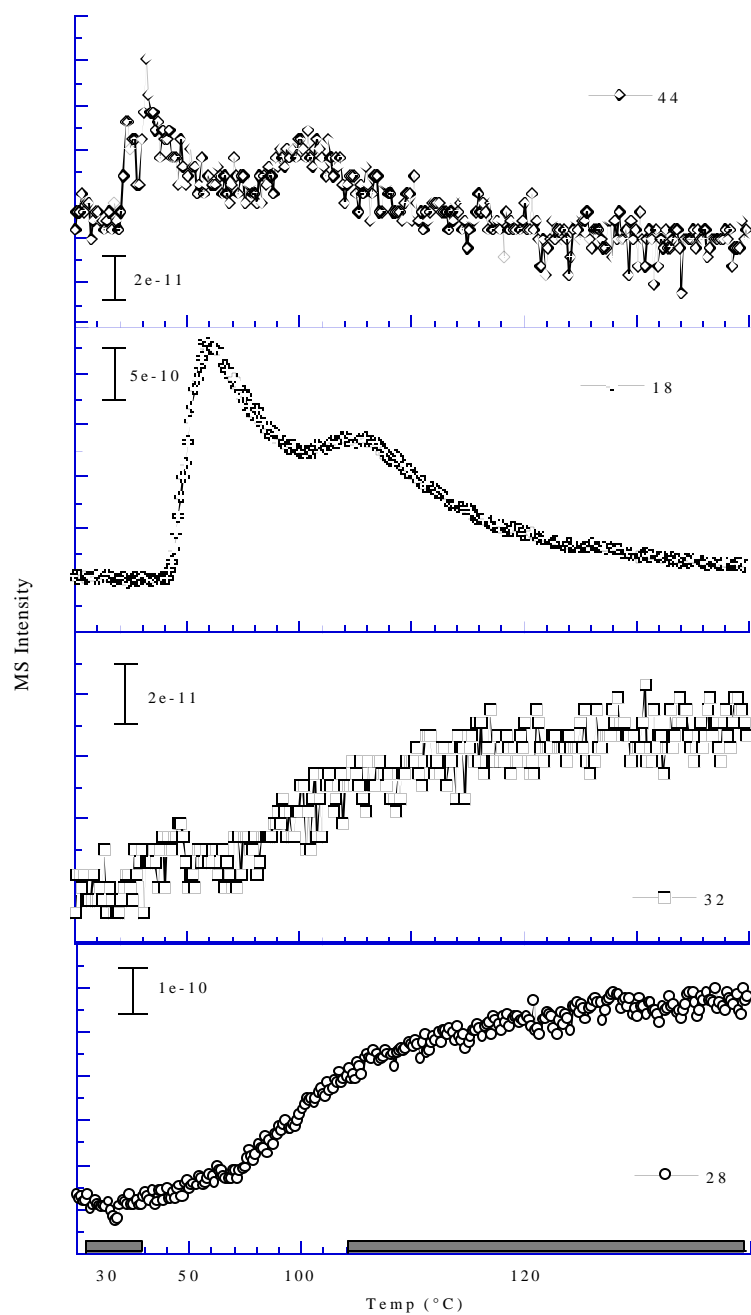


Figure 3. [MS analysis of the CO<sub>2</sub> TPD over 95C in He flow.]

Figure 4 illustrates the IR results of the TPD over the 95C run. As H<sub>2</sub>O evolved from the surface of the sample, CO<sub>2</sub> was concurrently released. While H<sub>2</sub>O was present on the sample, the adsorbed species decreased only slightly with increasing temperature (Figure 4). Shortly after reaching 120 °C a substantial amount of H<sub>2</sub>O had been removed and the adsorbates vanished. Similarly to the results illustrated in Figure 2 where we show that adsorption of CO<sub>2</sub> does not take place in the absence of water, a separate experiment (not shown) confirmed that desorption of CO<sub>2</sub> cannot take place in the presence of H<sub>2</sub>O. To further investigate the stability of the surface amine species, adsorption and desorption was repeated over used Sample 95C. Adsorption and desorption of CO<sub>2</sub> onto this regenerated sample were comparable to those of the fresh sample. Figure 5 illustrates the IR results from the TPD over the regenerated 95C. Once again, the adsorbed mono/bidentate carbonates were removed shortly after 120 °C was attained.

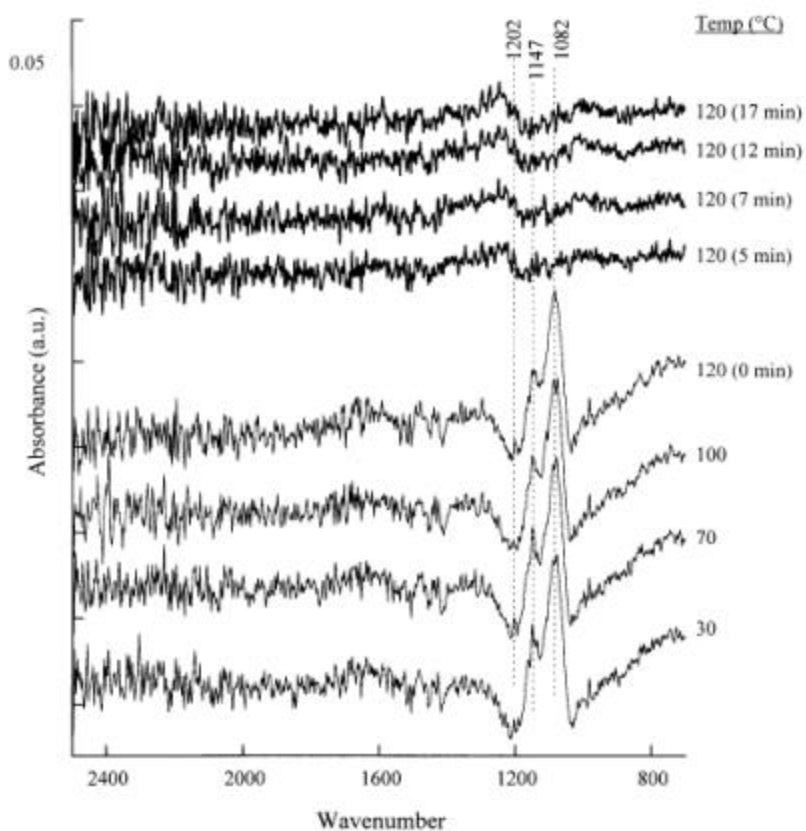


Figure 4. [IR analysis of the CO<sub>2</sub> TPD over Sample 95C]

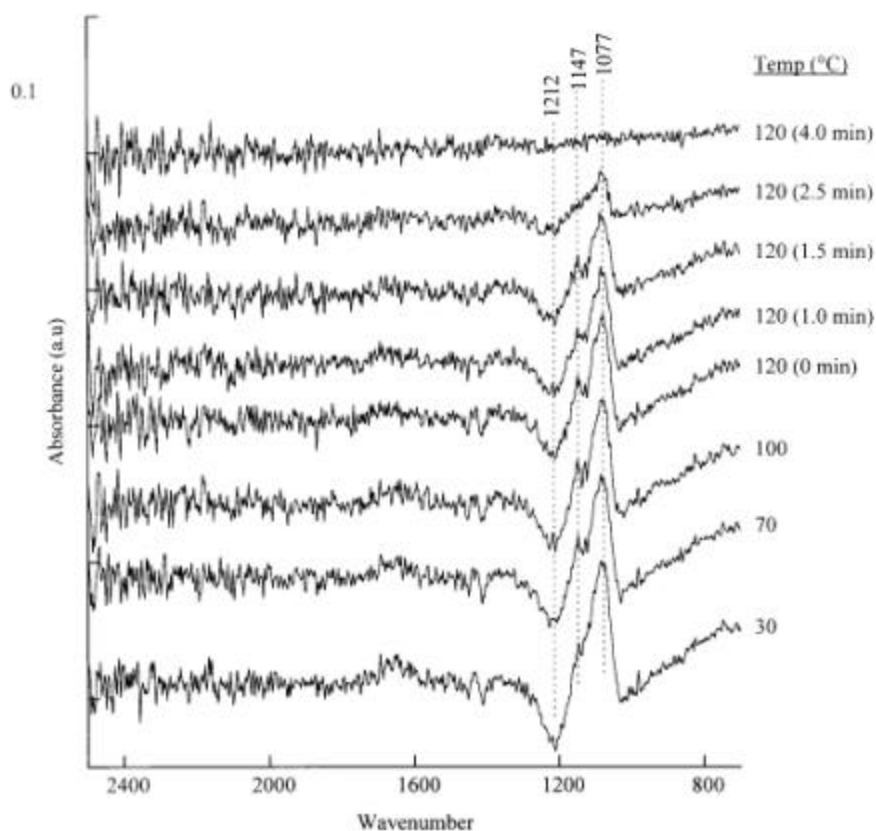


Figure 5. [. IR analysis of the CO<sub>2</sub> TPD over Regenerated 95C]

A summary of the CO<sub>2</sub> capture amounts is shown in Table 1. Samples 59 and 95 showed some CO<sub>2</sub> capture capability and were probably in the forms of physical/chemical adsorption of CO<sub>2</sub>. Treating Sample 95 with various chemical techniques (i.e., 95A, 95B, 95C) led to a significant enhancement of the CO<sub>2</sub> capture capability. Overall, Sample 95C performed best; capturing more than double the amount of CO<sub>2</sub> when compared to its untreated precursor. Regenerated 95C showed only a slight degradation in its CO<sub>2</sub> capture ability when compared to a fresh sample (140.6  $\mu\text{mol/g}$  vs. 174.5  $\mu\text{mol/g}$ ). This suggests that treatment “C” leads to fairly stable amine species on the sorbent surface. Nevertheless, the fly ash carbon only has a surface area of 30 m<sup>2</sup>/g. It is possible to apply the developed treatments to other high surface area substrates (e.g., molecular sieve, silica gel and

activated carbon). The success of bonding amine to these substrates may have the potential to develop effective sorbents for CO<sub>2</sub> capture.

*Table 1.* [Table 1. Amine-Enriched Sorbent Properties]

Sample #	Treatment methods	Nitrogen, %	Oxygen, %	CO <sub>2</sub> released $\mu$ mole/g sample
59(7% carbon)	none	0.21	0.61	24.4
95(52% carbon)	none	0.60	0.77	72.9
95A(52% carbon)	A	0.73	2.81	81.1
95B(52% carbon)	B	0.66	1.78	117.9
95C(52% carbon)	C	0.65	2.28	174.5
95C(repeated run)	C	0.65	2.28	140.6

In addition to desorption of CO<sub>2</sub>, species with  $m/e = 28$  (CO or N<sub>2</sub>) and 32 (O<sub>2</sub>) were observed to evolve at higher temperature and attained a steady state concentration in the reactor effluent (Figure 3). If the  $m/e = 28$  profile represents N<sub>2</sub>, this profile would be indicative of surface amine decomposition. It is also reasonable that this profile may be representative of CO, which would result if the complexed CO<sub>2</sub> species decomposed to CO and O on the surface. The fates and origins of  $m/e$  of 28 and 32 are still under investigation.

In summary, we have demonstrated that a carbon concentrate derived from fly ash can be transformed into a potential sorbent for CO<sub>2</sub> capture via the appropriate chemical treatments. The amine-enriched samples chemically adsorb CO<sub>2</sub> and water upon contact with a gaseous stream, thereby forming the amine complexes. An increase in temperature drive the reaction between the carbon dioxide, water, and amine in the reverse direction, thereby regenerating the amine and releasing the absorbed carbon dioxide and water.

## 4. CONCLUSIONS

Three different amine treatment procedures were applied to a carbon concentrate derived from fly ash. The direct reaction of CO<sub>2</sub> with the amine-derived substrate indicated some CO<sub>2</sub> capture capacity. Amine-enriched sorbents, with further modification, have the potential to be used as a sorbent for capture of CO<sub>2</sub>.

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